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NASA TM X-53676

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**A PRELIMINARY EVALUATION OF SILANE
COUPLING AGENTS AS PRIMERS AND
ADDITIVES IN POLYURETHANE
BONDING PROCEDURES**

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NASA

FACILITY FORM 602

68-13510 (ACCESSION NUMBER)	_____
15 (PAGES)	_____
TMX-53676 (NASA CR OR TMX OR AD NUMBER)	_____
	(THRU)
	1 (CODE)
	18 (CATEGORY)

*George C. Marshall
Space Flight Center,
Huntsville, Alabama*

GPO PRICE \$ _____

CFSTI PRICE(S) \$ _____

Hard copy (HC) 3.00

Microfiche (MF) .65

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ABSTRACT

Significantly improved strength retention at temperatures up to 200°F has been observed for polyurethane bonded joints in three bonding procedures where silane coupling agents were used as primers for metal adherends and in another procedure where a silane coupling agent was used as an additive to the resin system. Notable strength gains were also evident in bonds tested at cryogenic and ambient temperatures.

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PROPULSION AND VEHICLE ENGINEERING LABORATORY
RESEARCH AND DEVELOPMENT OPERATIONS

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SUMMARY

The polyoxytetramethylene based polyurethane adhesives are widely used for cryogenic applications but are markedly deficient at temperatures above ambient. A group of three commercially available silane coupling agents was evaluated as primers for aluminum adherends bonded with polyurethane adhesive, and one of the group was further tested by direct addition to the polyurethane resin to give an integral blend.

Vitally improved bond strengths were obtained in all tests at 200°F, a temperature near the upper useful limit for polyurethane structural bonds. Increased strengths were also obtained at cryogenic and at ambient temperatures. The overall joint improvements recorded in these tests strongly indicate that the use of silane coupling agents will effect impressive gains in strength and reliability of polyurethane bonded joints.

INTRODUCTION

The polyoxytetramethylene based polyurethanes; i.e., Adiprene L-100, Narmco 7343, Products Research 5211, and 3M XC-3515, comprise a class of adhesives in general use for structural bonding in areas subjected to cryogenic temperatures. Strengths of aluminum-to-aluminum bonds fabricated with these adhesives are very high at the temperatures of liquid hydrogen (-423°F) and liquid nitrogen (-320°F), but notable strength decreases accompany a rise to ambient temperatures and above. Further characteristics of the polyurethane adhesives are the wide scatter that is often observed within a given set of lap shear tensile or T-peel specimens tested at a given temperature, and the wide variation between average strength values obtained from different sets of specimens.

This publication presents the preliminary results of attempts to improve the higher temperature utility and overall reliability of the polyurethane adhesives by application of silane coupling agents to the adherends in a priming technique or by addition of silane coupling agents directly to the polyurethane resin system. Narmco 7343, cured with MOCA (4,4'-methylene-bis(2-chloroaniline)) is representative of the polyurethanes and is the specific example of its class in the results reported here.

DISCUSSION

Three commercially available silane derivatives were evaluated as primers for cleaned aluminum adherends. These were:

- a. Dow Corning's Z-6040 (hydrolyzed with acetic acid before application)
- b. Dow Corning's Z-6020
- c. 3M Company's XC-3901.

The first material listed, Z-6040, was also evaluated for direct addition in small percentages to the polyurethane resin system just before application of the adhesive to the clean, unprimed metal surface.

Tables I and II show the average values obtained from standard lap shear tensile and T-peel specimens fabricated from 2014-T6 aluminum sheet with the Narmco 7343/MOCA (100 g/11.5 g) adhesive systems. All of the data presented are of relatively recent origin, collected since August, 1966. During this period, an insufficient number of T-peel specimens was tested to establish statistical veracity for the tabulations of Table II; however, the available data, as presented, are suggestive of the peel strength improvements to be expected when silane-type primers or additives are used.

Figures 1 and 2 are bar graphs of the lap shear tensile and T-peel data, respectively. It is immediately apparent that silane coupling agents are responsible for significant strength gains in both lap shear tensile and T-peel test configurations. Particularly revealing is the evidence that Dow Corning's Z-6040 adhesive proved highly effective when incorporated at the one percent level directly into the resin system.

Table III shows the percent strength improvement over the lap shear tensile control series when silane type additives and primers are used. Table IV shows similar results for T-peel configurations, but it should be emphasized again that only a small number of T-peel specimens has been tested.

The additive technique and the three priming formulations each produce positive benefits, particularly in the troublesome region around 200°F. The hydrolyzed Z-6040 primer system appears to promote the best overall performance, but a simple addition of non-hydrolyzed Z-6040 directly to the adhesive resulted in significant improvements at all test temperatures and no priming of the metal was required.

Table V shows data obtained from a series of 300 lap shear tensile specimens, of which half were bonded with a 1.2 percent Z-6040 additive formulation and the remainder with a standard control formulation. At room temperature, inclusion of Z-6040 improves bond strengths and yields a 50 percent reduction in mean variation between the single high and single low specimens. The outstanding effect of Z-6040 at 200°F is to raise the average value to nearly four times that of the average control value. Furthermore, even the lowest single measurement from the Z-6040 modified formulation is twice that of the highest single control specimen. This improvement in the +200°F problem area is particularly desirable.

RESULTS AND CONCLUSIONS

The performance of polyurethane bonded aluminum-to-aluminum joints was notably improved in three cases when commercially available silane coupling agents were evaluated as primers for the adherend surfaces and in another case when one of the materials was used as an additive to the polyurethane resin system. Increased bond strengths were obtained at -300°F, at room temperature, and at +200°F. The improvement at +200°F was the most pronounced, and coincidentally, the most coveted, since polyurethane adhesive performance at that temperature has always verged on the unacceptable. Particularly attractive is the prospect of employing selected silane coupling agents as additives to the resin system, thus eliminating a metal priming step in the bonding procedure.

These results should in no way be taken as a final assessment of the silane coupling agents available to adhesive technology or the optimum manner of their utilization in bonding procedures. These data from a limited number of evaluations, however, are compelling evidence that routine use of silane coupling agents in standard polyurethane bonding procedures will greatly enhance the strength and reliability of the bonded joints.

EXPERIMENTAL

Metal Preparation.- Aluminum adherends (2014-T6 alloy) were given a standard sulfuric acid-sodium dichromate etch. Lap shear tensile specimens were fabricated from 0.063-inch sheets and T-peel specimens from 0.020-inch sheets.

Adhesive Formulation and Cure.- In a typical adhesive formulation, 11.5 grams of MOCA was added in a molten state to 100 grams of Narmco 7343 resin. Bond line thickness was regulated by incorporation of glass

beads, 0.003-inch to 0.005-inch, into the adhesive mix. Cure cycle was 48 hours at room temperature, followed by 24 hours at 160°F.

Z-6040 Additive.- One gram of Z-6040 was stirred into 100 grams of Narmco 7343 resin just prior to addition of the curing agent.

Z-6040 Primer.- Solution A - 49.50 g H₂O
0.50 g acetic acid
5.00 g Z-6040

Solution B - 2.20 g Solution A
90.00 g Methanol
8.00 g H₂O

Solution B was brushed onto the metal surface immediately after preparation. The primed surface was allowed to air dry at room temperature for two hours.

Z-6020 Primer.- Z-6020 (0.20 g) was added to absolute ethanol (99.80 g). The solution was immediately brushed onto the metal surface, which was then air dried for one hour at room temperature.

XC-3901 Primer.- XC-3901 was brushed directly onto the metal surface and allowed to air dry for one hour.

TABLE I.- EFFECT OF SILANE PRIMERS AND ADDITIVES ON LAP SHEAR TENSILE VALUES

Primer	Lap Shear Tensile, psi, At Test Temperature					
	R.T.	N**	-300°F	N**	+200°F	N**
No primer (control)	1626	150	6517	40	464	75
No primer, 1.0% Z-6040 Additive	2234	150	9151	45	1691	150
Hydrolyzed Z-6040	2847	65	8624	55	2027	60
Z-6020	3325	40	9115	40	1401	40
XC-3901	2310	35	9105	30	1383*	30

* 180°F

** N = number of specimens averaged.

TABLE II.- EFFECT OF SILANE PRIMERS AND ADDITIVES ON T-PEEL VALUES

Primer	T-Peel, piw, at Test Temperature					
	R.T.	N**	-300°F	N**	+200°F	N**
No primer (control)	33.7	6	19.9	6	20.9*	6
No primer, 1.0% Z-6040 additive	35.3	6	39.7	6	26.7	6
Hydrolyzed Z-6040	51.5	6	61.3	6	36.2	6
Z-6020	22.2	18	59.5	18	30.2	18
XC-3901	29.7	12	25.2	12	39.9*	12

* 180°F

** N = number of specimens averaged.

TABLE III.- LAP SHEAR TENSILE STRENGTH GAINS ATTRIBUTED TO USE OF SILANE ADDITIVES AND PRIMERS

Test Temperature	Percent Improvement over Lap Shear Tensile Control Series			
	1% Z-6040 Additive	Z-6040 Primer	Z-6020 Primer	XC-3901 Primer
Room Temperature	37%	75%	104%	42%
-300°F	40%	32%	40%	40%
+200°F	264%	337%	202%	198%

TABLE IV.- T-PEEL STRENGTH GAINS ATTRIBUTED TO USE OF SILANE ADDITIVES AND PRIMERS

Test Temperature	Percent Improvement over T-Peel Control Series			
	1% Z-6040 Additive	Z-6040 Primer	Z-6020 Primer	XC-3901 Primer
Room Temperature	-7%	36%	-41%	-21%
-300°F	100%	208%	199%	26.6%
+200°F	28%	73%	44%	90%

TABLE V.- EFFECT OF Z-6040 ADDITIVE

Adhesive Mix	Lap Shear Tensile, psi, at Room Temperature				
	N	Low	High	Average	Mean Variation %
Control + 1.2% Z-6040	75	1560	2210	1844	-16 +20
Control	75	990	2080	1490	-33 +40
	Lap Shear Tensile psi at +200°F				
Control + 1.2% Z-6040	75	1270	2370	1713	-26 +39
Control	75	346	604	464	-25 +30

Notes: (1) Control - 100 grams Narmco 7343, 11.5 grams MOCA.

(2) N = number of individual specimens averaged.

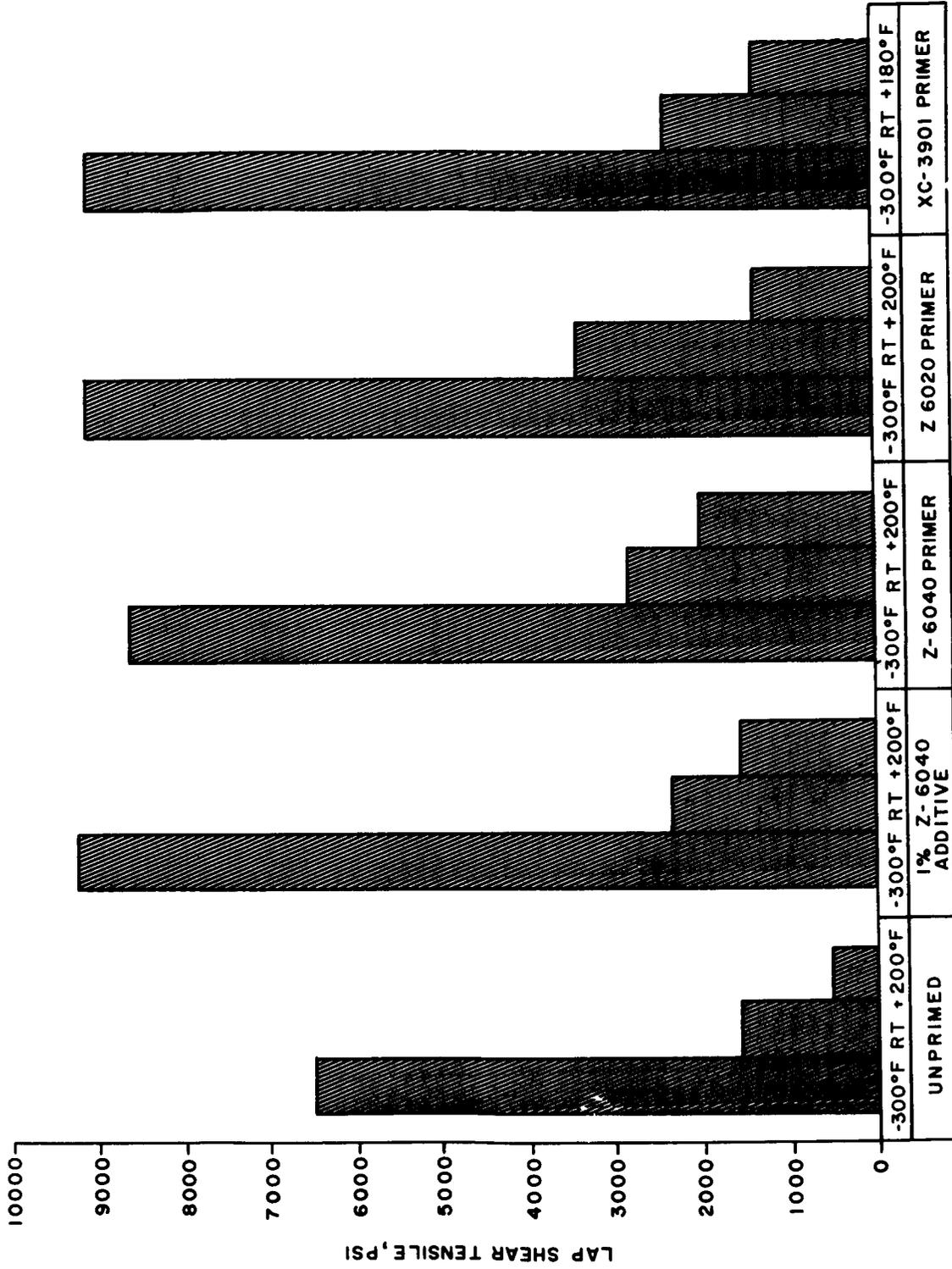


FIGURE 1.- EFFECT OF SILANE PRIMER AND ADDITIVES ON LAP SHEAR TENSILE STRENGTH

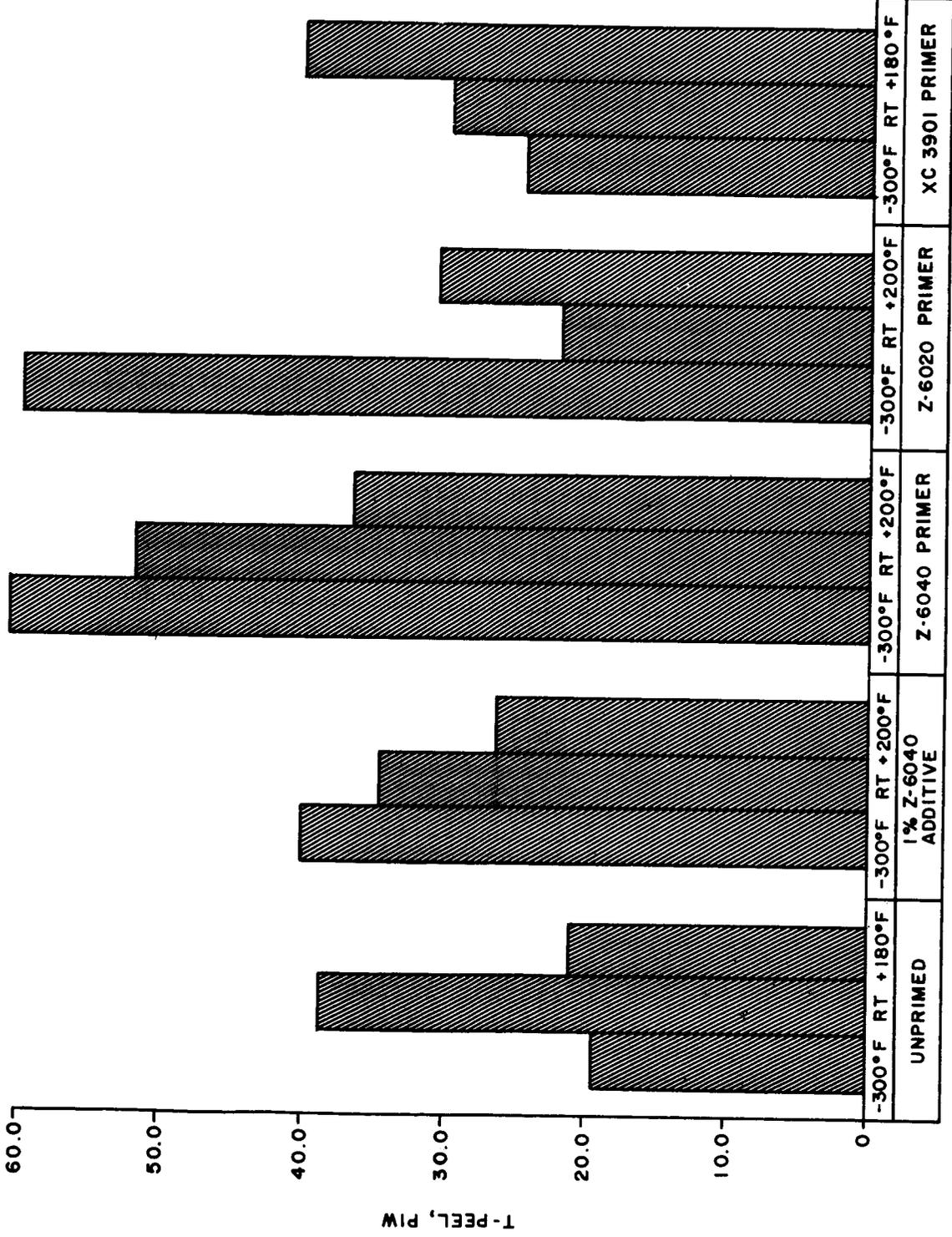


FIGURE 2. - EFFECT OF SILANE PRIMERS AND ADDITIVES ON T-PEEL STRENGTHS

November 28, 1967

APPROVAL

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The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

This document has also been reviewed and approved for technical accuracy.



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November 28, 1967

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